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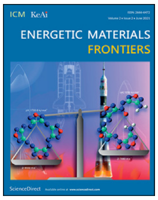

Ageing studies on AP/HTPB based composites solid propellants

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ABSTRACT

Components of solid rocket motor that are susceptible to ageing are propellant, insulator, inhibitor, interfaces, igniter system, and seals. Seals, insulator, ignition systems are replaceable but the motor would be recast when the deterioration in propellant and liner are beyond specified limits due to the ageing. There is a large body of literature available on the ageing of composite solid propellant, each focusing only on a particular type of ageing in propellants rather than having a synergistic view of the various different ageing processes and hence the literature looks disconnected. Further, there are a few studies which are still classified and are one of the reasons for the above disconnect. This review paper is an attempt towards establishing the bridge among these studies. Different types of ageing: physical, chemical ageing, hygro-chemical ageing and the deterioration associated with cumulative damage have been discussed in detail. The ageing related deterioration plays an important role in the safe-life estimation of solid propellant based rocket motor. Therefore, sources and mechanisms of ageing have been explored and their associated effects on the propellant properties (physical and mechanical) are also described. A summary on accelerated ageing methods which are typically followed to study thermo-chemical ageing of propellants is presented in this paper. Studies related to the degradation of propellant-liner interface are also reviewed. Advances in health monitoring (passive and active) of stored grains have been visited. Further, the gap in propellant ageing research have been identified and suggestions are provided for the future research.

1. Introduction

Solid rockets might be the oldest chemical propulsion systems in the human history. Their mentions can be traced back to 1200 AD when the Chinese repelled the Mongol invaders by their ‘arrows of flying fire’ or possibly much earlier when the Chinese started using a simple form of gunpowder made from saltpeter (potassium nitrate), sulphur, and charcoal dust to create fireworks during their festivities.[1] On the Indian sub-continent, Hyder Ali and Tippu Sultan were the first to use rockets in the 18th century against the British army.[2] Sir William Congreve improved these rockets which were subsequently known as Congreve rockets.[3] The science behind the rocketry has evolved over centuries since the earliest usage of gunpowder based fireworks to the modern rocketry. The modern rocketry was established by Konstantin Tsiolkovsky in 1903. Subsequently, the solid rocket has evolved due to the need for better missile defense systems and space exploration.

In both defense and space applications, a solid propellant based rocket motor is preferred over a liquid/hybrid rocket motor due to the following advantages: simple construction, mobility, high thrust capability, readiness to launch on short notice and relatively moderate storage conditions. Solid propellant is a solid phase mixture of oxidizer and fuel which releases the required energy for propulsion on combustion. Solid propellants are broadly classified into two categories namely: ‘homogeneous’ and ‘heterogeneous’ propellants. In a homogeneous solid propellant, fuel, oxidizer, stabilizer and plasticizers are mixed at the molecular level to form a colloid and the ingredients are indistinguishable after mixing. Depending upon the number of active substances (that release energy upon combustion) in the composition, a homogeneous solid propellant can be single-base, double-base or triple-base. Double-base propellants are used in anti-tank missiles and short-range surface-to-air missiles. Composite solid propellants (CSPs) are the heterogeneous multi-modal mixtures of oxidizer (micron size particles), binder (polymer based), metal & metalloid fuel additives, plasticizers, chain extenders, ballistic modifiers and antioxidants. Composite solid propellants are frequently used for long-range strategic missiles due to the steady burning rate, higher specific impulse, and higher specific density.[4,5]

1.1. Composite solid propellants

Composite solid propellants evolved along with the development of

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their binder system. Primarily, a binder system consists of a liquid prepolymer and a curing (cross-linking) agent. The binder system holds together all the ingredients of CSPs to forms a particulate composite, provides the required mechanical properties to the composite and also acts as a primary fuel. Non cross-linked binders (e.g., asphalt) used during World War II had a very narrow temperature operation range and slumping issues in large diameter motors. In 1940s, cross-linked binders (such as polysulphide, polyester, polyurethane, polystyrene based) were introduced and further developed to meet the service needs of higher flexibility, higher solid loading and a wide operating temperature range. Polybutadiene based binder systems were introduced due to their compatibility with Al (aluminum), a fuel additive and higher flexibility at low temperature conditions. Among them, polybutadiene acrylic acid acrylonitrile (PBAN) and carboxy terminated polybutadiene (CTPB) were extensively used till the late 1960s. However, they suffered variation in initial mechanical properties due to the variations in cross-linking sites. Since the early 1970s, hydroxyl-terminated polybutadiene (HTPB) became the principal prepolymer for binder system due to easy curing process (even at a lower temperature), reproducibility, good mechanical properties over wider temperature range and better ageing properties.[2,4,6–8]

Typically, plasticizer and other additives like chain extender, ballistic modifier, bonding agent, antioxidant are introduced, before the polymerization, to enhance the properties of the binder system. Plasticizer (e.g., dioctyl adipate (DOA)) is used as an additive to increase flexibility of polymeric chains and to improve rheological properties during the propellant mixing process. Metal particles of micron size (e.g., aluminum, magnesium) acts as secondary fuel and increase the combustion temperature leading to higher specific impulse. Metal oxides (e.g., Iron oxide) and metalloids (e.g., Boron, Magnesium) are also added as combustion catalysts.

In practice, ammonium or potassium perchlorate, ammonium or potassium nitrate are some of the oxidizers utilized in producing CSPs. In most cases, ammonium perchlorate (AP) is preferred due to its density, thermal stability and higher proportion of oxygen. However, the use of perchlorate leads to serious environmental issues such as ground water contamination (may lead to thyroid cancer), ozone layer depletion and increase in acid rains due to the formation of large quantities of hydrochloric acid on combustion. Therefore, there has been a quest for a green oxidizer which has a lower environmental impact and plume signature. Ammonium nitrate (AN), ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are promising chlorine free oxidizers, developed in the recent past.[9] Conventionally, AN is used in nitrogenous fertilizers and industrial explosives. AN finds application as an oxidizer for solid propellant due to its lower cost, lesser & cleaner combustion byproducts and simpler handling & storage (less sensitivity to friction and impact). However, AN based propellants tend to have near room temperature crystallographic phase transition, limited range of burning rates and do not support efficient burning of Al.[10,11] ADN and HNF are considered as possible replacements of AP due to higher burning rates and specific impulse.[9,12,13] However, they pose challenge in handling and storage as they are sensitive to shock, light and moisture.[9,13] Further, HNF requires newer processing methods to handle its incompatibility with the conventional HTPB binder system.[9,12]

After the typical mixing process, the CSP is either directly cast (vacuum or injection) into a rocket case for case-bonded grain or in a cylindrical mould (that also acts as a burning inhibitor) for a free standing grain which would be loaded as cartridge in a rocket case at later time. For a case-bonded grain, thermal insulator, inhibitor and liner are pre-installed in the motor case prior to the casting. The liner acts as a bonding interface between the insulator and the propellant. Case-bonded grain configuration is preferred for large rocket motors.[4,5,14]

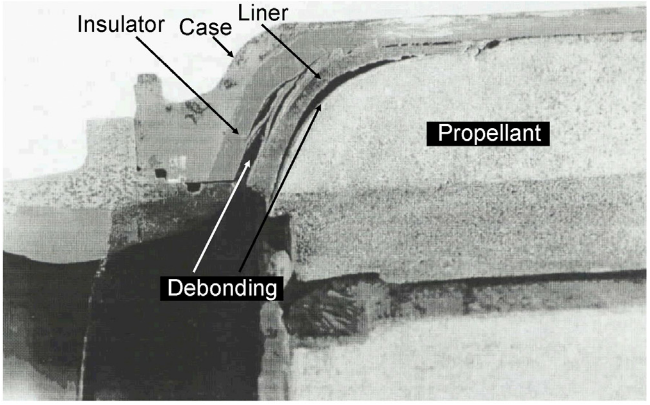
1.2. Ageing

Ageing refers to the deterioration in the physical, ballistic and mechanical properties with time which is driven by the changes in physical characteristics, chemical composition or thermodynamic state due to interaction of the material with the environment.[15,16] Solid rocket motors are produced in large numbers, are stored for many years and are usually transported to different harsh & remote launch sites before their intended usage. Typically, the minimum service life requirement of any solid rocket motor is 10 years after casting of the propellant and/or after assembly of the rocket motor. Although the assembled rocket motors are stored under controlled conditions before the actual use in a missile, the grain experiences mechanical, thermal and vibratory loads and its chemically active ingredients interacts with the environment (temperature, oxygen, etc.). Under these conditions, they are expected to have a long shelf-life. However, both the homogeneous and composite propellants are found to be susceptible to ageing during the long storage period.

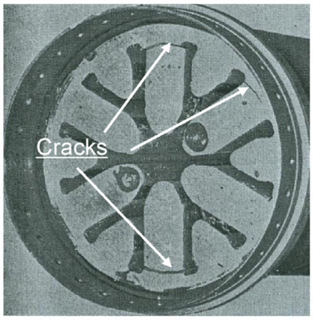
Ageing in a solid propellant grain is found to be slow and complex due to various influencing factors and resulting mechanisms. Different failure modes such as formation of cracks, debonding at interface, migration and slump (excessive deformation) were observed in aged rockets during inspections.[17,18] Fig. 1 depicts some of these failure modes. Even in the absence of such damages (macroscopically invisible), there are also incidences of significant deviation in the ballistic performance from the design values, due to the migration of chemically unbonded ingredients.[19] Therefore, understanding the ageing phenomenon of the solid propellant and rocket motor interfaces are essential in determining the in-service time (or shelf-life) of a rocket motor.

The available literature indicates that AP, Al and HTPB have established themselves as the leading oxidizer, fuel and binder system for CSP grains used in large rocket motors. Henceforth in this paper, a detailed review on the ageing of AP/HTPB and AP/Al/HTPB based CSP is presented. Since the mid-1970s, researchers have been studying the ageing of AP/HTPB based CSPs and hence, there is a large body of literature available, whereas limited literature is available on ageing studies of rocket motor interfaces which is equally important to estimate the service life of rocket motors. The purpose of this paper is to give a comprehensive summary connecting these works, observe the ageing effects on the performance properties of the CSP and suggest some future research areas on this broad topic.

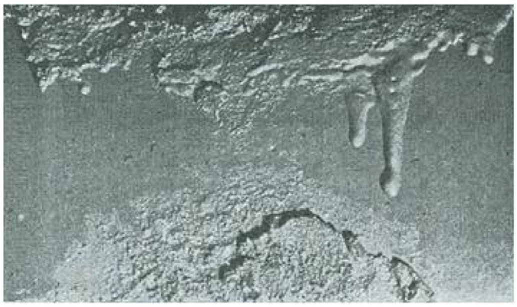
The ageing study of a solid rocket motor consists of experimental studies on specimens representing individual components, sub-systems and full scale motor by means of natural ageing and accelerated ageing techniques. Consequently, the ageing methodology involves evaluation at four different levels, as indicated in Fig. 2. At Level-1, tests are carried out on representative specimens of individual materials: propellant, insulator and inhibitor. Level-2 involves study of propellant-insulator, propellant-inhibitor and motor-insulator interfaces. The specimens for Level-1 (individual components) and Level-2 (interface) studies are drawn from cartons. Cartons are blocks of propellant or propellant-liner interfaces (typical size of 300 mm × 300 mm × 180 mm) cast along with actual rocket motor casting, or for every new propellant composition trials, in order to check the batch properties of the rocket motor. At Level-3, the studies are carried out on Proto-type motors: (a) sub-scale motors simulating the critical interfaces that dominate the service life of rocket motor; (b) Lambda motors designed such that thrust-time profile matches with the actual full-scale motors and (c) ballistic evaluation motors which are cast for every new batch of propellant composition to evaluate its ballistic properties. The final stage of evaluation is studies on the full-scale motors, i.e., Level-4. At this stage, periodic health monitoring (surveillance) of the actual motors is carried out by visual inspection, Ultrasonic Testing (UT) and radiography. Mechanical and ballistic properties are evaluated from motor dissections and static firing of the actual motor at periodic time intervals. Studies at all the levels need to be carried out on specimens, cartons and motors aged naturally to understand the ageing phenomenon. However, natural ageing happens over an extended time period and the results are not available in timely manner to enable prediction of useful life of the rocket motor. Consequently, accelerated ageing under elevated temperatures using various methods



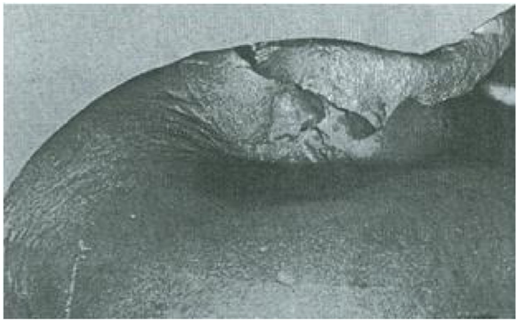
(a) Debonding



(b) Crack formation



(c) Migration of ingredients



(d) Slump deformation

Fig. 1. Typical failure modes in grains due to ageing: (a) debonding between liner and grain, (b) crack formation, (c) migration of the ingredients and (d) slump deformation.[20,21] (Image reprint permission was obtained from the original publisher.).

(as described later) is carried out at Level-1, Level-2 and Level-3. However, to validate the developed accelerated ageing methodologies, degradation during accelerated ageing has to be correlated with natural ageing studies at all levels.

In literature, three different types of deterioration processes in CSP have been reported, namely: (a) physical ageing (b) cumulative damage and (c) chemical ageing. In the following sections, these processes have been studied in detail and their respective impacts on the physical and mechanical properties of the CSP are discussed. Physical properties like density and hardness are quality check measurands and could indicate the grain deterioration during periodic checks. Mechanical properties like stiffness, tensile strength, percentage elongation, relaxation modulus, etc., are used in the stress/strain analysis of the grain, subjected to various types of loads from its cast to firing. Ballistics properties: burn rate, energetic and specific impulse are very critical parameters which dictate the mission trajectory and performance of the motor. Any significant deviation in these properties from the specified values would be a threat to the rocket/launch mission. Any debond at the interfaces and cracks in the grain due to ageing would lead to an increase in the propellant burn rate locally and could cause instability, eventually leading to a catastrophic failure of the rocket motor itself.

2. Physical ageing

When a polymer is quenched below its glass transition temperature, it changes from rubbery state to glassy state (molecular chain rearrangements). There is a significant loss in mobility of molecular chain and its segments, however, the mobility does not cease. During this process, the polymer reaches thermal equilibrium with it surroundings before it reaches its thermodynamic equilibrium (Fig. 3a). Over a period of time, it slowly evolves (relaxes) towards its thermodynamic equilibrium under no mechanical load, accompanied with the changes in free volume, enthalpy, entropy and mechanical properties. This process is termed as physical ageing. Physical ageing is a thermo-reversible phenomenon and involves no chemical modification, e.g., breaking/forming of atomic bonds or permanent modification of the chain structure.[22]

2.1. *Physical ageing related to glass transition*

The thermograms (obtained using differential scanning calorimetry (DSC)) of HTPB based binder system exhibit several thermal transitions in temperature range of −100 °C–100 °C (Fig. 3b). The lower temperature transition is associated with glass-to-rubber transitions of the soft HTPB segments and the higher temperature transition is related to glass-to-rubber transitions of the hard HTPB segments.[23] The above mixed soft and hard segments are the typical chain structure of HTPB based binder system. The soft (long) segments are the main chain elements and hard (short) segments are the cross-links.[24] The lower glass transition temperature of the cured HTPB is around −70 °C which gets marginally reduced (more negative) due to the addition of chain extenders and particles (AP/Al).[23,25] Therefore, the physical ageing associated with the lower glass transition temperature of the CSP is not a concern during the storage period. However, the higher temperature transitions (>-20 °C) of the CSP may be a concern for the low temperature storage locations. Moreover, the relaxation process of the hard HTPB segment becomes complex due to the presence of particles which significantly affect the mobility of hard segments and introduce damping in the network.[25]

The literature on the physical ageing associated with the hard segment of the CSP is limited. Researchers[25–28] studied the thermal transitions and morphological/structural changes in the HTPB based CSPs using dynamic mechanical analysis (DMA) under cyclic loading and low strains. Nevertheless, the above mechanical loading might influence the relaxation process related to the physical ageing. In the constant frequency–temperature sweep DMA test, loss factor variation curve had two distinct maxima (Fig. 4a) which were related with the relaxation events in the chain structure. The first peak (narrow) indicated the lower glass transition temperature of the CSP and was referred as α-transition. The second peak (broad) was called β-transition and was related to the motion of short-hard-segments. Bihari et al.[28] have indicated that β-transition might occur above 0 °C. Further, the complete binder network would also be affected by curing stress (section 3.1) and chemical ageing (section 4), causing increase in the cross-link density

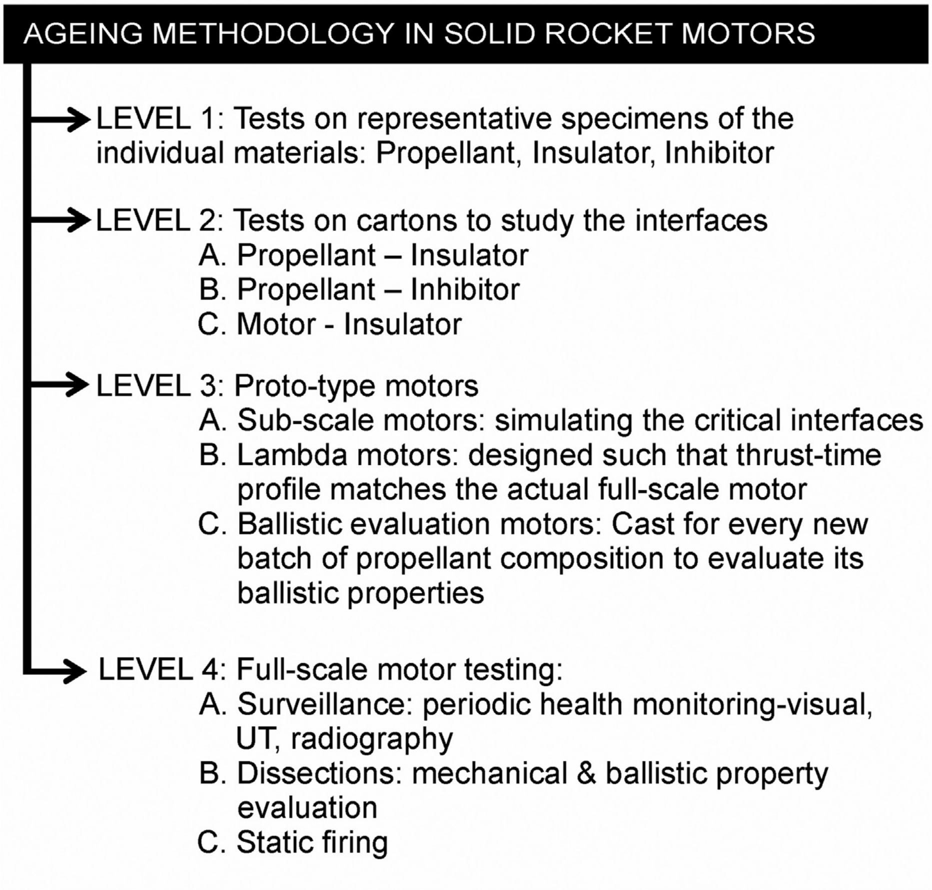

AGEING METHODOLOGY IN SOLID ROCKET MOTORS
LEVEL 1: Tests on representative specimens of the individual materials: Propellant, Insulator, Inhibitor
LEVEL 2: Tests on cartons to study the interfaces
A. Propellant – Insulator
B. Propellant – Inhibitor
C. Motor - Insulator
LEVEL 3: Proto-type motors
A. Sub-scale motors: simulating the critical interfaces
B. Lambda motors: designed such that thrust-time profile matches the actual full-scale motor
C. Ballistic evaluation motors: Cast for every new batch of propellant composition to evaluate its ballistic properties
LEVEL 4: Full-scale motor testing:
A. Surveillance: periodic health monitoring-visual, UT, radiography
B. Dissections: mechanical & ballistic property evaluation
C. Static firing

Fig. 2. Ageing methodology for evaluation of the ageing in composite solid propellant based rocket motors.

during storage. de la Fuente[25] have also demonstrated that the glass transition of the soft segments increased due to isothermal ageing at 65 °C. Therefore, there is a scope to study the physical ageing in CSP grain for low temperature storage condition and its influence on the mechanical and ballistic properties.

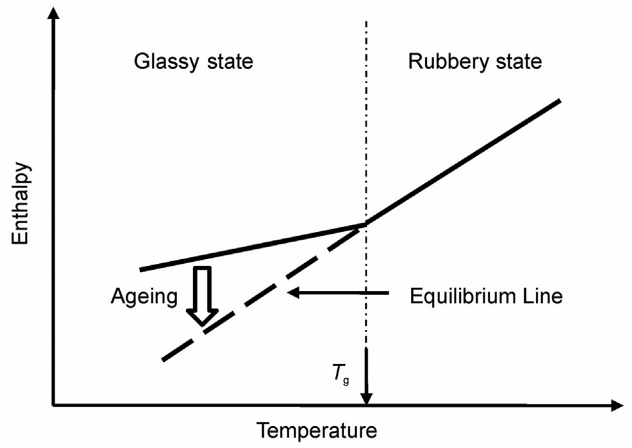
2.2. *Physical ageing due to migration of chemically unbonded species*

In the CSP based motors, there is another prevailing form of physical ageing. It is related to the motion of few chemical species within the polymer network and to the diffusion/absorption of foreign species (solvent or water) in the network and is also referred as physico-chemical degradation.[29] During the CSP manufacturing, the plasticizer is added to lower glass-to-rubber transition temperature (for better lower temperature storage) and to improve the pot life of propellant slurry and strain capability of the propellant. It also enhances the flexibility of bulk propellant, especially at low temperatures. However, the plasticizer is not chemically bonded to the binder network and tends to migrate after the cure period as well. In case-bonded grain, there could be inter-migration of plasticizer and curing agent (during the curing period) between liner and grain beside the above intra-migration of plasticizer (Fig. 4b). Further, moisture present in the ambient of the propellant grain could diffuse into the grain and could lead to both the physical and chemical ageing. Moreover, moisture can also be present as a contamination during the propellant manufacturing. The above migration and diffusion would change physical (swelling/shrinking & softening/hardening of liner/propellant), mechanical & ballistic properties of the propellant and adhesion properties at the liner-propellant-insulator interfaces. Various studies on the plasticizer, catalyst, curing agent migration and moisture/water diffusion have been discussed in the following paragraphs.

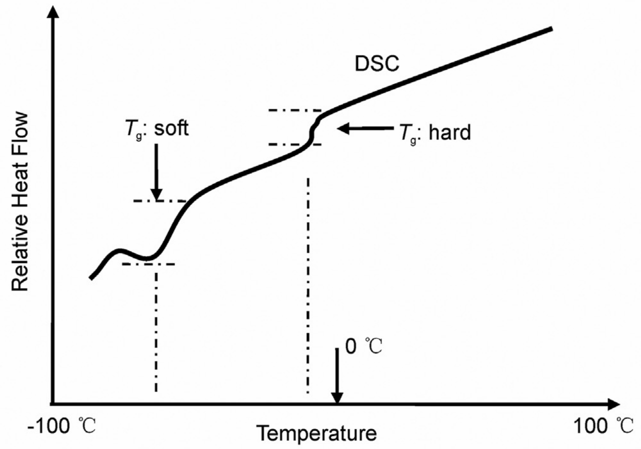
Dee et al.[30]; Probster and Schmucker[19]; Venkatesan et al.[31] reported that the tendency to migrate was strong near liner-propellant grain interface and the migration rate reduced with increasing distance from the interface (i.e., towards the core). It occurs because liner is also a polymeric material that contains plasticizer of different concentration. Inter-migration of plasticizer from liner to propellant grain and vice versa during the storage period caused changes in characteristics of the propellant, insulator and their interfacial bonding. The migration of plasticizer increases burn rate which leads to coning in the end burning grain and pressure peaks at the end of quasi-steady combustion in the core burning grain. Probster and Schmucker[19] suggested that the plasticizer migration could be contained or minimized by proper grain distribution during mixing and by increasing cross-link density.

Gottlieb and Bar[32] studied the intra and inter migration of DOA in the cast propellant through Fick's law based diffusion process. They confirmed that the plasticizer migration had significant effects during the curing period and the initial period of ageing. However, once homogeneous concentration was reached, plasticizer migration is minimized. They also suggested that the plasticizer migration would be overtaken by other ageing mechanisms during the long storage period. Their diffusion-based plasticizer migration model was verified by Libardi et al.[33] for other plasticizers. Judge[34] showed that the degree of propellant/grain confinement has significant effect on the plasticizer loss during the ageing and suggested that a weather-sealed rocket motor would not suffer plasticizer loss during the storage. In literature, various other techniques such as periodic rotation of the motor, use of migration barriers and chemical bonding of plasticizer with binder network were employed to alleviate some of the physical ageing effects.

Various researchers have established that AP particle size and multimodal particle packing have decisive effect on the burn rate and



(a) Physical ageing



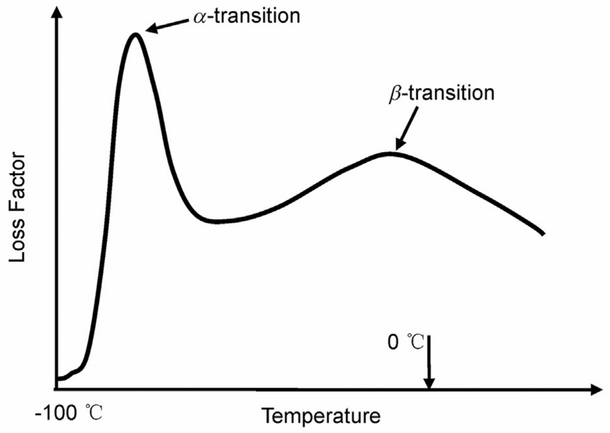
(b) DSC thermogram

Fig. 3. (a) Change from rubbery state to glassy state and (b) Differential scanning calorimetry (DSC) thermogram showing the thermal transitions.

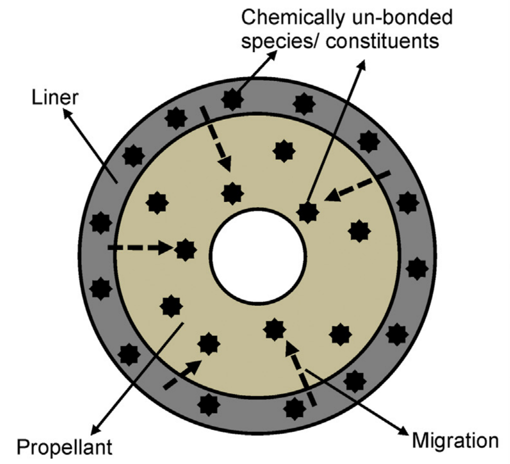
combustion characteristics of the CSP. AP is a hygroscopic, soluble in water and forms agglomerate on humidity exposure which leads to increase in AP particle size and change in the particle morphology.[35] Bunyan et al.[6] reported that the moisture could initiate recrystallization and form agglomerates of small oxidizer (AP) particles. Humidity diffusion in the grain could lead to poor oxidizer surface, porosity and shrinkage which could cause dewetting at the oxidizer/binder interface and reduction in burn rate.[17,35] Moisture exposure also causes chemical ageing and has been described in section 4.

3. Cumulative damage

A composite solid propellant behaves as a non-linear, thermo-visco-elastic material which exhibits time-temperature history dependent response and undergoes finite deformation upon loading. When a CSP is loaded, small micro-structural damages occur within the material and weakens it for the subsequent loadings. These damages get accumulated upon repeated loading/unloading and continuously reduce the load/deformation bearing capacities of the material. The above deterioration is referred as cumulative damage phenomenon or mechanical ageing.[36,37] During the storage period, a propellant grain experiences various load and temperature histories due to post curing cooldown, ambient temperature diurnal variation, bulk load, transportation and handling. All these loading cases contribute to the cumulative damage of the CSP which is further worsen due to the ongoing physical (section 2) and chemical (section 4) ageing.



(a) DMA transition curve



(b) Migration in rocket

Fig. 4. (a) Schematic of loss factor variation curve obtained from DMA showing the thermal transitions and (b) schematic of inter-migration/diffusion of chemically unbonded constituents (*e:g:*, plasticizer/curing agent) from higher concentration to lower concentration in a rocket motor.

The cumulative damage leads to failure: cracks in the grain, debonds at the interface with liner and excessive deformation of grain. For propellant grains, various cumulative damage assessments based on Miner's law[38] and its derivative: linear cumulative damage model[39] are found in literature. However, most of these studies focus on the damage associated with the environmental temperature variations and corresponding service-life prediction (section 3.3). Service-life prediction (or reliability assessment) of a grain follows probabilistic approach due to the variability present in the induced loads and material properties, both of them considered as random variables.[21] In the following sections, literature on the cumulative damage of a CSP grain and service-life prediction models have been discussed with respect to the different load/temperature histories.

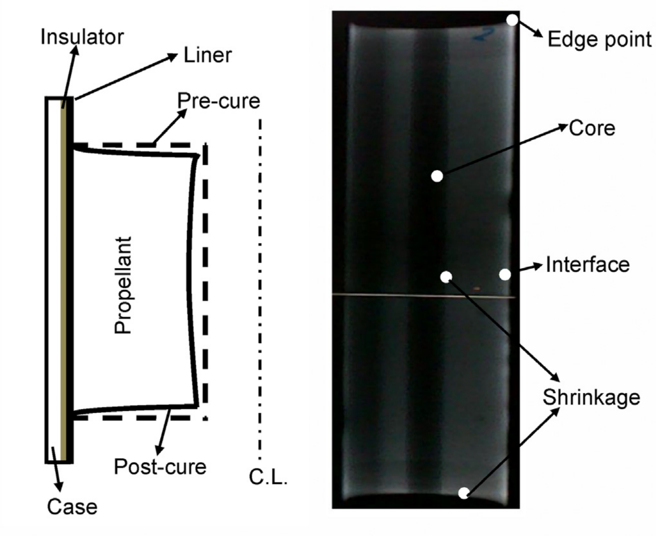
3.1. Residual stress due to cooldown after the cure

AP/HTPB based propellant is typically cured at around 60 °C and the grain is assumed to be in stress-free state at this temperature. After the cure, the grain is allowed to cool naturally or at a slower rate to the ambient temperature, for ensuring uniform temperature in the grain. During this cooldown, the free-standing grain encounters only thermal strain and no stress due to thermal contraction (or shrinkage). However, a case-bonded grain experiences thermal stresses due to its constrained geometry and the mismatch between the coefficients of thermal expansion of case, liner and propellant. The coefficient of thermal expansion of the solid propellant and liner are typically an order of magnitude greater than that of the case material. Therefore, the grain and liner would shrink to a greater degree than the case which would restrain the grain/liner shrinkage. This would result in significant thermal stress at the case/grain interface and becomes of larger concern in large size motors. Moreover, the grain also experiences biaxial stresses at the inner-bore surface during this restrained shrinkage.[4,37,40,41] Fig. 5 shows the schematic of the post cure propellant shrinkage and associated deformation.

In earlier studies, analytical solutions for stress and strain fields for a composite cylinder: representing a core burning grain with case, were obtained under plain strain conditions using thermo-elasticity.[43] Both the case and the propellant were considered linear elastic. End effects (3D effects) were included through length-diameter ratio parametric curves and the stress concentration pertaining to various port designs was accounted using photoelasticity.[44,45] The time-dependent behavior of the propellant was modeled using linear viscoelasticity and correspondence principle. The propellant response was captured through spring dash-pot combinations.[14] Later, these analyses were refined and improved employing finite element method and more realistic material models.[42] This provided an estimate of the stress/strain field in the grain after the cure. The above state became the reference state for the subsequent loading cases. Further, fibrous composite cases allowed curing under pressure and minimizing the residual shrinkage stress/strain for small/-medium sized motor.[4]

3.2. Slump

A large composite solid propellant grain is prone to creep or excessive deformation (slump) due to its viscoelastic nature, large bulk load, dynamic loads sustained during transportation and long storage period. Slump due to short time-high acceleration loads during flight have not been considered in this review. Although the induced stresses due to the above loads are small in magnitude, their cumulative effects during long storage period may be significant. A motor may be stored in horizontal or vertical position with different support conditions. In vertical position, the slump tends to increase the grain port diameter near the throat when there is no end support (Fig. 6a). Otherwise, the slump would tend to choke the nozzle throat due to port bulging near to the end support (Fig. 6b). Fig. 6c shows the slump deformation in the port of a horizontal motor which would incite port blockage.



(a) Cooldown shrinkage (b) X-ray image of a grain

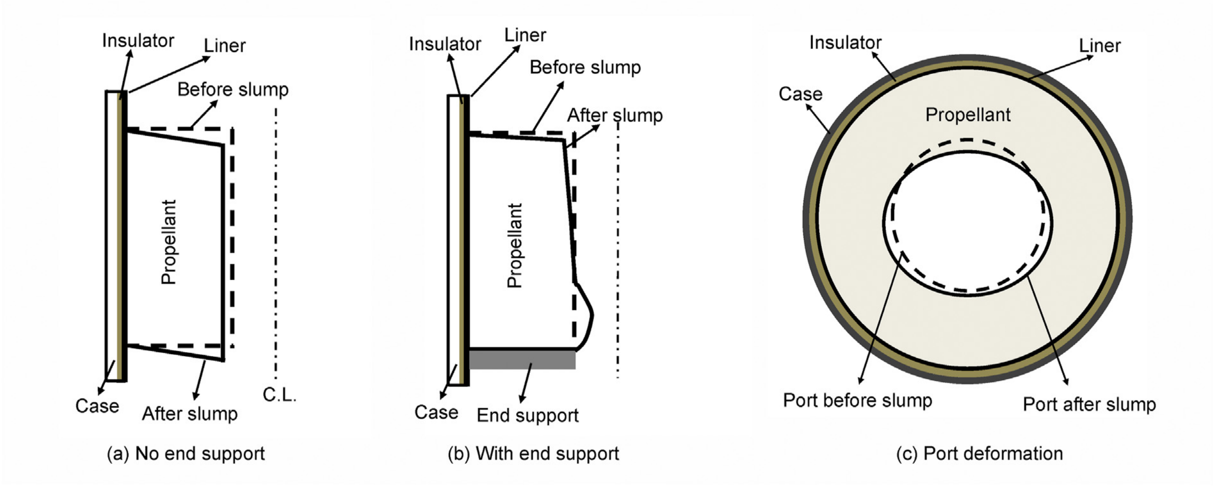
Fig. 5. Schematic of the longitudinal cross-section of a case-bonded grain before the start of the curing and at end of the cooldown[4]; (b) X-ray image of a cured grain showing shrinkage post cooldown.[42] (Image reprint permission was obtained from the original publisher.).

Similarly, a motor may be subjected to intermittent, random vibration while transportation/handling and consequently exhibit slump (Fig. 1d). Moreover, extended period of vibration may also lead to cracks in the grain, softening of the propellant and migration of chemically unbounded ingredient to the free surface.[20] Auto-ignition may also get triggered due to internal heating and slower heat dissipation (owing to lower thermal diffusivity of the propellant) during the excessive vibration. The above cases of slump deformation affect motor internal ballistics and may lead to phenomenon called structural ballistic interaction,[21] henceforth, need to be predicted during the grain design. Typically, internal support structure is provided in the motor case to keep the slump deformation within the limit for larger grains. Moreover, the stored motor is periodically rotated to minimize the slump. High frequency and long-time period vibratory loads are avoided during transportation and ground handling.

Knauss[46] presented approximate solutions (both the elastic & time dependent material) for slump displacement in the vertical storage position. Boyd et al.[14] found considerable slump deformation in a large sized grain in a rigid case, when stored in vertical position with no end restraint. They have estimated the critical slump deformation of 0.327 inch after 100 min of storage for a large size motor (15 feet diameter & 53 feet length). They had used four-parameter spring-dashpot model (linear viscoelastic) to represent the creep response of the propellant over long time and hence suggested an appropriate support structure to reduce the slump deformation. Slump deformation for a long, viscoelastic port-burning grain (in rigid case) stored in horizontal position was obtained by Lianis.[47] In continuation, Herrmann and Tamekuni [48] considered the finite length grain with curve and flat end and showed that longitudinal & circumferential shear stresses at the liner-grain interface were much higher in the finite length grain.

However, the above solutions did not consider different port geometries which could only be addressed through finite element analysis (FEA). Renganathan et al.[49] performed FEA of a large, port-burning grain in a maraging steel case with no end support and the FEA based estimation of slump deformation matched well with the measured slump. Nawaz and Nizam[50] estimated the slump deformation for grains (linear viscoelastic) with the star-port geometry in both the horizontal and vertical positions with no end supports. They have also performed cumulative damage study for the grain when it was stored in different positions sequentially. Deng et al.[51] analyzed the creep deformation of an actual 3D grain (non-linear viscoelastic) due to long-term storage of 10 years coupled with chemical ageing.

Ostrem[52] provides a good resource for estimating (theoretical) vibratory loads experienced by the grain during the transportation and handling events. Every event of these loadings affects the stress/strain state of the grain and contributes to cumulative damage. To obtain the above state, material model under the dynamic loading is required. Like other materials, CSPs also respond differently under the dynamic loads as compared to static or quasi-static loads. Tormey and Britton[20] have studied the effect of cyclic loading on propellant material response. They reported softening of propellant under extended vibration condition and a portion of hardening was regained during the given rest period. Wang et al.[53] have conducted uniaxial tests under low to moderate strain rates (up to 14.14 s^{-1}) and developed a non linear viscoelastic constitutive model incorporating the damage as a parameter. Open literature on propellant testing/response under dynamic load/high strain rates is sparse. In their service-life assessment of a solid rocket motor, Yılmaz et al.[54] have shown that the damage induced due to the vibratory loads were not negligible for the chosen transportation and handling histories. They have reported that cumulative damage due to cyclic thermal stress is 20.8% and cumulative damage due to vibration is 1.55%. Moreover, they have used a linear viscoelastic constitutive material model



(a) No end support (b) With end support (c) Port deformation

Fig. 6. Schematic of excessive deformation of grain when the grain is stored in vertical position (a) without end support; (b) with end support and (c) port deformation when stored in horizontal position.[43]

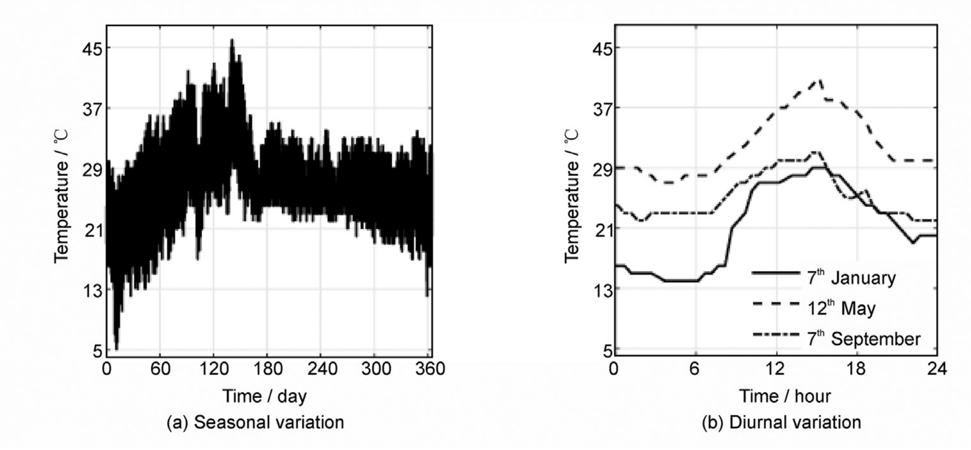
developed for quasi-steady loading. Therefore, reasonable constitutive models of the propellant response under dynamic loading are required to assess the micro/macro material damage during transportation and handling events.

3.3. Cyclic thermal stress due to ambient or environmental temperature variation

Ambient temperature of a storage location has seasonal and diurnal variations. Fig. 7 represents these variations in the ambient temperature of a given storage location during a year. These variations in the ambient temperature are pseudo-cyclic in nature and are superimposed upon each other. The diurnal variation (high frequency component) has time period of 24 h and the seasonal variation (low frequency component) has time period of 1 year.[55] The above temperature variations produce thermal stresses and strains in the viscoelastic grain encased in metallic or composite case due to the mismatch in coefficient of thermal expansion and thermal diffusivity of case and grain respectively. The cyclic thermal stress is obtained in two steps: (a) temperature distribution in the grain due the given boundary conditions; (b) thermal strain and subsequently thermal stress developed due to geometrical constraint and thermal gradient. Temperature controlled storage or encapsulation of rocket motor using thermally insulated material reduces cumulative damage due to cyclic thermal stress.

Geckler[56]; Mahmoudi and Atefi[57] estimated thermal stresses in grain without case under periodic temperature boundary conditions. Zwick[58]; Zak[59]; Tunc et al.[60] calculated thermal stresses and deformation in grain with case under periodic/arbitrary temperature boundary conditions. Heller et al.[55] obtained the thermal stress and strain in the long hollow thick cylinder (plane strain) with an outer insulation layer, under environmental temperature variation. Thangjitham and Heller[61] have presented a comprehensive procedure to calculate temperature, thermal stress and strain in a core-burning viscoelastic grain encased in a metallic case (plane strain) stored under outdoor storage conditions. The thermal loads included the variations of ambient temperature, sky radiation, wind convection and solar radiation. Each cycle of the above thermal stresses (loading/unloading) is associated with the ambient temperature and would cause a small damage in the thermo-viscoelastic grain. The cumulative damage due the repeated cyclic thermal stresses will result in failure of the grain. The following paragraphs summarize various cumulative damage assessment studies predicting failure in the grain caused by environmental temperature.

Heller et al.[55] studied the failure of a long core-burning elastic grain encased in an insulated case (plane strain) due to environmental temperature using probabilistic approach. They considered the statistical variability of thermal load, strength and strain capacity. Power spectrum of thermal load was derived from 10 years time-temperature data. Results showed that the diurnal temperature variation caused significant thermal gradient at the web whereas seasonal temperature variation gave rise to high tangential stress at the bore and radial stress at the grain-case



(a) Seasonal variation (b) Diurnal variation

Fig. 7. Seasonal and diurnal variations in ambient temperature of a storage location.

interface. In continuation, Heller and Singh[62] have improved the above service-life predictions by modeling the grain as a viscoelastic material and including the effects of chemical & mechanical (stress induced deterioration) ageing on the mechanical properties. Similarly based on probabilistic failure criteria, Gligorijevic et al.[36,63,64] showed that environmental temperature could cause significant cumulative damage leading to cracks in a grain within short period of shortage. Moreover, Gligorijevic et al.[36] have used natural ageing data to include the chemical ageing effects on the mechanical properties.

Using the first-passage method, Zibdeh and Heller[65] have also predicted service life of a long, hollow grain (viscoelastic) encased in an insulated case and subjected to cyclic thermal stresses due to environmental temperature and chemical ageing. Thermal loads corresponding to a hot and a cold location were selected and service life was found to be shorter at the cold site. Janajreh et al.[66] used first-order second-moment reliability method to predict the service life of an insulated-encased grain. This method correlated modulus and strength properties which were considered independent (with their variations) in the previous studies and were leading to more conservative estimates of service-life. Further, the ambient temperature was effectively represented only by its seasonal and diurnal variations, reducing the computational cost. The service-life prediction requires a reasonably accurate determination of stress & strain (at region of interest) in the grain stored under environmental thermal conditions, and a statistical model of the propellant strength & strain capacity. The determination of stress/strain depends on the statistical representation of thermal load and material constitutive model. During the storage, Margetson and Wong[67] measured the above stress (interface), strain (bore) and temperature using sensors instead of estimating them using constitutive model. Subsequently, the measured data were analyzed to determine the time dependent statistical variation of the peak stress and strain response.

Ozupek[68]; Yıldırım and Ozupek[69] presented finite element based structural analysis procedure for a grain (aged/unaged; nonlinear viscoelastic) subjected to storage conditions, and deterministic approach based service-life prediction. The environmental temperature loads were modeled through the worst-case scenario (non-cumulative) defined by a two-step loading cases: 50 °C to mean temperature and mean temperature to -32 °C. Propellant capabilities (strength and strain) against the predefined failure modes: cracking at bore due to tensile strain and debonding at liner-insulation interface, were obtained experimentally using strip and wedge tests. Yılmaz et al.[54] proposed reliability based service-life assessment methodology for an encased grain (linear viscoelastic) subjected to environmental thermal (including seasonal and diurnal variations) and vibratory loads. Uncertainties in material properties and chemical ageing (Layton's model[70]) were considered. Results showed that the thermal loads (diurnal temperature amplitude $\leq$5 °C) caused significant cumulative damage (>20%) during long storage period (40 years).

3.4. *Studies on cumulative damage at interfaces*

In the rocket motor, the interfaces involving propellant, liner, insulation and case are considered to be the critical failure locations. Propellant-liner is most critical transition interface and is highly strained while storage and firing. Compatible liner compositions are derived based on propellant polymer (HTPB) to achieve adequate interface properties.[71] Zhou et al.[72] provided a comprehensive review on these interfaces in terms of their adhesive properties, adhesive mechanisms, ingredients migration, damage determination and fracture analysis. Kakade et al.[73] carried out experimental evaluation of interface bond strength and effect of ammonium perchlorate (AP) particle size on the interface properties. They also carried out accelerated ageing studies of interface samples at 50 °C for 6 months and found cohesive failure in propellant. They observed that as the percentage of AP increases, peel strength value decreases.

In a large solid rocket motor, this interface varies from igniter location to nozzle location (Fig. 8). As the web thickness of the grain varies in these locations, the thermal stresses induced at these locations also differ. Minuteman propulsion surveillance program[74,75] presented an approach to ageing studies of large solid rocket motors. It has considered ageing studies on components, sub-scale motors and full-scale motors. Failure models were categorized with respect to age sensitivity and mission criticality. The only realistic approach to estimate the service life is dissection of samples from full scale motor at different time periods and testing of the same. Analytical models were developed and validated using material property data at sample level.

Liu and McCamey[76] discussed on bondline interfaces of the solid rocket motor. The review emphasized that full scale motors are key components of a successful ageing program and modeling of accurate and correct environmental exposure of rocket motor for laboratory samples. Differences always exist between cartons and rocket motors with respect to polymeric system, cast geometry, size, flow characteristics, variability etc. Variability in gradients within the cartons and gradients within the motors, variability in ageing environments and variability in component populations were key attributes in evaluating margin of safety for the rocket motors. Further it has been observed that though propellant strength was consistent between motors and cartons, strain was generally much lower within a rocket motor than that obtained from carton data. Also, Young's modulus for propellant in rocket motors was considerably higher than that obtained from carton data. Mere use of chemical kinetics alone provides incomplete picture of actual ageing of rocket motor. Significant gradients in mechanical properties near bond interface due to chemical reactions or migration of species within the rocket motor were observed. Hence these stresses must be simulated in the laboratory samples.

4. Chemical ageing

The ingredients of CSPs remain chemically active throughout the shelf life of the propellant grains. The reactive state permits various chemical reactions over time in the presence of different stimuli like ambient temperature, humidity, air and ultraviolet radiation (UV). These chemical reactions are typically irreversible and cause significant deterioration in the propellant properties. The deterioration associated with the above chemical reactions is referred to as chemical ageing. The influences of the above stimuli are minimized by storing the free-standing grain in metal/composite weather-sealed cases or by installing pressure membrane in case-bonded grain motor. However, even under standard propellant storage conditions, the grain is susceptible to ambient temperature variations due to its size and long storage duration. The ambient temperature (with its seasonal & diurnal fluctuations) acts as an incessant ageing stimulant for the chemical (also called natural) ageing of propellants. Therefore, in the past, researchers have extensively studied the chemical ageing of propellants, stimulated by the ambient temperature. These studies were focused on understanding the degradation mechanisms and their impact on various propellant properties. Therefore, some researchers studied the chemical ageing of AP/HTPB & AP/Al/HTPB based CSPs as a complete system while other researchers preferred to study the binder systems alone since the binder system provided the required mechanical properties to the CSP and was severely affected by ageing.

At ambient temperature, natural ageing processes are slow chemical reactions. Therefore, artificial (laboratory) ageing methods are employed to accelerate these reactions and to study their long term effects on the propellant properties within a reasonable time period. To intensify the effects of temperature stimulant, the propellant samples are stored at higher temperatures (than ambient) for shorter durations. On completion of the accelerated ageing, the aged samples are tested to measure a predecided property of the propellant and the change in this property is recorded with respect to the unaged samples. Further, Arrhenius or Berthelot equation[77] is employed to extrapolate the above change in the property from short duration– high temperature ageing to obtain the

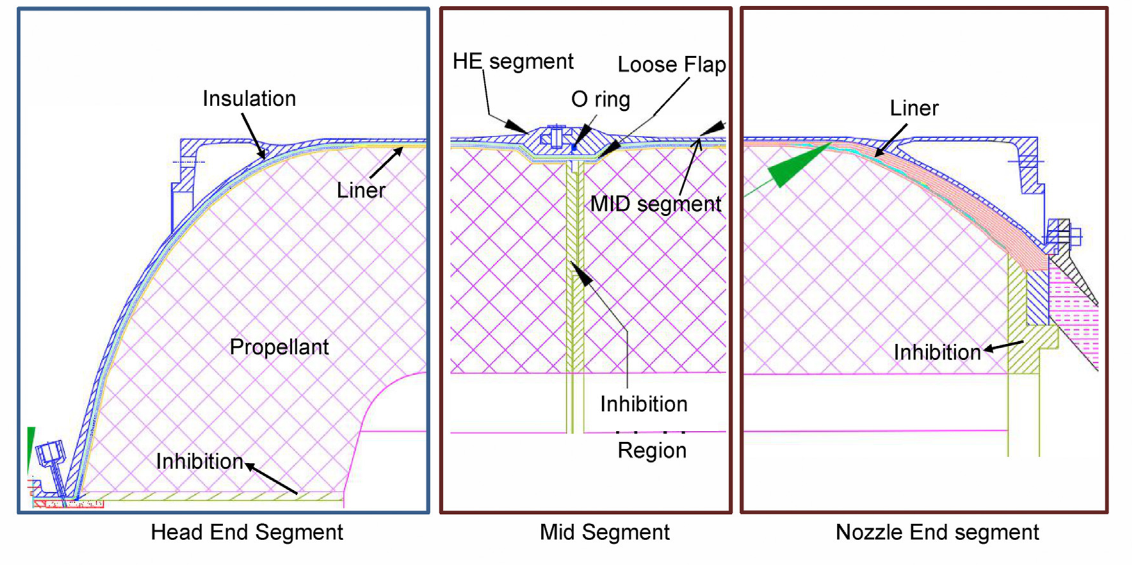


Fig. 8. Variation in propellant and its interfaces across the length of the motor.

corresponding change in the property when the grain is stored for long duration at ambient temperature. The details of the above artificial ageing methods are described in the following section and chemical ageing of CSPs (temperature and moisture) and only binder system are presented in the subsequent sections.

4.1. Artificial accelerated ageing methods

In literature, the following three types of artificial accelerated ageing methods are reported: (a) isothermal, (b) non-isothermal (rate type), and (c) cyclic ageing.

4.1.1. Isothermal ageing method

In isothermal ageing method, samples are kept in an oven at constant temperatures (T_o) higher than the actual service/storage temperature, represented by the constant annual ambient mean values (T_s). After different time intervals (t_o) corresponding to different ages (t_s), these samples are tested and change in a chosen property (P) is recorded. The shelf-life is estimated from the above ageing data (t_o, $\Delta P(T_o)$) using Layton's ageing model[70] or thermal equivalent load principle[27] or time-temperature rate equations such as Berthelot or Arrhenius equations.[78] Typically, the following form of Arrhenius equation is used to correlate accelerated ageing condition (t_o, T_o) to storage/service condition (t_s, T_s) for the given allowable change in the property.

$$\ln(t_s) = \ln(t_0) + \frac{E}{R}\left(\frac{1}{T_s} - \frac{1}{T_0}\right) \tag{1}$$

Where R is the universal gas constant and E_a is the apparent activation energy of the degradation processes (natural ageing). The above correlation assumes that the same degradation processes are occurring at T_o & T_s. However, there are many examples of non-Arrhenius behavior in literature, if T_o is much higher than T_s.[79,80] In the above equation, E_a is unknown and is estimated as follows. From the above ageing data (t_o, $\Delta P(T_o)$), t_os and corresponding T_os are obtained for various percentage changes in the property. The slope of $\ln(t_o^{-1})$ plotted against $1/T_o$ for the different percentage changes in the property provides the value of E_a.[81] Judge[34] has provided the apparent activation energy of the natural ageing processes for AP/HTPB based CSP as 71–74 kJ·mol^{-1} and Shekhar[77] has reported the activation energy for AP/Al/HTPB based CSP as 72.8 kJ·mol^{-1}. Celina et al.[82] have also provided a similar approach based on the shift factor to estimate E_a. Shift factor correlates different time-temperature-property data with respect to a reference temperature.

4.1.2. Non-isothermal ageing method

The isothermal method requires a few months to get a useful life estimation. Hence, there was a need for faster methods like the non-isothermal method. In this method, E_a of the degradation process is obtained through thermal analysis techniques such as thermo-gravimetric analysis (TGA; ASTM E1641) and differential scanning calorimetry (DSC; ASTM E698). They are frequently used to obtain kinetic parameters including E_a of degradation and decomposition processes occurring at higher temperature (>200 °C). Subsequently, one elevated isothermal ageing is performed and the service life is predicted using Eq. (1). Flynn[83–85] have critically discussed the implementation, limitations and common drawbacks of using thermal analysis techniques for lifetime prediction. In case of composite solid propellants, researchers have indicated that natural ageing processes might be the dominant till 60 °C–70 °C.[24,34,82,86] DSC and TGA are not very sensitive up to 100 °C, therefore, non-isothermal method was found to be ineffective for estimating apparent activation energy of natural ageing processes of CSPs. Nevertheless, non-isothermal method has been successfully used for lifetime estimation of other polymeric materials.[83,87]

4.1.3. Cyclic-thermal ageing method

Noticeably, either of the above methods does not consider the diurnal and seasonal variations in the ambient temperature (the stimulant). Recently, Naseem et al.88 have developed cyclic-thermal ageing method for accelerated ageing of propellants. The method accounted for the variations in the stimulant and also related the natural ageing of propellant grain with accelerated ageing of the propellant samples. The diurnal ambient temperature variations at a given location in a year were processed to obtain a characteristic diurnal variation (high frequency component), which was augmented with ambient mean (T_m) of each day to include the seasonal variation (low frequency component). This process provided 365 cycles of natural ageing stimulant corresponding to each day in a year. To constitute the accelerated ageing cycle, the intensity of the natural ageing stimulant was amplified by a ΔT_m increase in its mean with an accompanied reduction in its time period. Shortened time period (τ_a) of the accelerated ageing cycle, for a chosen ΔT_m, was estimated using a modified form of Arrhenius equation while ensuring that the quantum of damage was same during the natural and accelerated ageing. Heat transfer analysis of the propellant sample was performed to ensure that τ_a is large enough to subject its entire volume to same temperature cycling (homogeneous ageing). The maximum temperature in the above accelerated ageing cycles was always kept below 65 °C to ensure that only natural degradation processes were dominant during the accelerated ageing.[88]

4.2. Ageing studies on composite solid propellant

In the chemical ageing of composite solid propellants, chemical reactions occur among the ingredients of the propellant in which ambient oxygen and humidity may participate. The ambient temperature acts a stimulant for these reactions under the storage conditions. In the following sections, literature on temperature assisted chemical ageing and the chemical ageing wherein ambient humidity is reacting with the constituents of the propellant are reviewed separately.

4.2.1. Thermo-chemical ageing

Layton[70] started the ageing studies of HTPB based composite solid propellants (CSP) and emphasized on chemical reaction kinetics during curing and ageing processes. The propellant was aged for 36 weeks at 23.9 °C, 43.3 °C, 57.2 °C and 65.6 °C on AP-HTPB based propellant with 88% solid loading. The objectives of this study were to understand the chemistry of ageing, correlate the chemical ageing results with the changes in mechanical properties and apply this understanding to other propellant systems. A technique was developed to separate binder (HTPB) during curing and ageing in terms of Sol (soluble or non cross-linked binder) and Gel (insoluble or cross-linked binder). Hence, the cross-linking was indirectly measured by the amount of gel. During curing, hydroxyl group of binder reacted with isocyanate (curing agent) and this curing reaction did not have any influence on the ageing reaction. The study showed that the percent gel increased as a linear function of logarithmic ageing time and the rate of increase was greater at elevated temperature. It was possible to extrapolate the 23.9 °C ageing curve to 32 years. However, there were no long time real (natural) ageing data available for this propellant for verification of the extrapolated result.

Christiansen et al.[89] extended Layton's study to higher solid loading range of up to 91%. They also verified his thermally accelerated ageing data with measured data of real ageing over six years. They concluded that the chemical reaction between AP and HTPB during ageing was the cause behind the change in the mechanical properties and the rate of this chemical reaction was controlled by the diffusion process. They observed that the deterioration rate due to ageing is slower in HTPB based propellant as compared to other binder systems like CTPB and PBAN. They attributed this reduced ageing effect to the coating of AP surface with HTPB.

Olson and Gill[90] measured the thermal decomposition rate coefficient of AP and the reactivity of HTPB individually and with the rest of the propellant ingredients. The thermal decomposition rate coefficient was measured by release of NH3 from small sample of AP at four temperatures between 71 °C and 107 °C, using NOx chemiluminescence monitor. The data were fit to Arrhenius equation with an activation energy of 123.8 ± 17.2 kJ·mol^{-1}. HTPB reactivity tests were performed on samples which were exposed to a reactive gas (N_2, air, NO, and a mixture of 5.5% of N_2 and 94.5% air) for 54 h at 71 °C. These reactivity tests involved measurement of weight gain/loss of binder, sol/gel analysis and molecular weight distribution analysis of the samples. The measured gain in weight of binder was due to the absorption of the reactant gases. Samples with AP or AP & Al showed an insignificant difference in the measured weight gain. Sol/gel analysis showed that the propellant with higher solid loading cured slowly. The sol content increased by roughly 70% in the samples with AP and increased by 2–3 times in the samples with AP/Al, irrespective of reactive gas environment. However, the authors doubted the sensitivity of the sol/gel analysis and molecular weight distribution analysis. Therefore, they recommended usage of more sensitive techniques to study the degradation of HTPB based propellants. They assumed that the binder degraded after reacting with the byproducts of decomposition of oxidizer. Earlier, Kishore et al.[79,91] had demonstrated that AP decomposition provided oxygen for oxidative degradation of another binder (polystyrene).

Bunyan et al.[6] also reported oxidative degradation (causing increase in cross-linking) of binder as the main contender for ageing along with recrystallization of AP (due to moisture) and migration of additives. They experimentally proved that the atmospheric oxygen is important for ageing. The increase in cross-linking density obtained using Charlesby-Pinner equation was higher for samples aged at higher temperatures. The variation in the cross-linking density was lesser and uniform in the case of the samples aged at a lower temperature for a longer period. The variation in the cross-linking density was steeper near the surface and shallower near the core in case of the samples aged at higher temperatures for shorter periods. These observations indicate that the change in cross-link density is due to diffusion-driven oxidation process and hence the surface is more prone to ageing. They also noticed that the use of the burn rate catalyst increased the cross-linking density near the surface of the propellant.

Hocaoglu[92] aged samples with different cross-link densities for 300 days at 65 °C. Various levels of cross-link density were achieved by changing molar ratios of isophorone diisocyanate (IPDI) to HTPB and antioxidant to HTPB. After every 30 days, uni-axial tensile tests and hardness tests were performed for four samples each. They observed that the samples with a higher ratio of IPDI to HTPB were more susceptible to ageing and deterioration. In the case of lower IPDI, a free radical mechanism drives cross-linking. They suggested that the decomposition of AP acted as a protonic initiator for the cross-linking reaction. The proton transfer mechanism due to its lower activation energy of $\approx$13 kcal/mol remains the main promoter for the increase in cross-linking.

Judge[34] conducted isothermal ageing of an AP/HTPB based CSP for 21 months at 38, 43 and 60 °C in semi-confined conditions to study the chemical kinetics and degradation mechanisms. He monitored modulus, strength, percentage elongation and sol-gel values and found that the oxidative cross-linking of the binder was the predominant degradation mechanism. Changes in modulus and soluble fraction were used to estimate the activation energy (71–74 kJ·mol^{-1}) of the propellant degradation.

Researchers also sought techniques which required comparatively lesser quantity of propellant for the ageing study like differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). de la Fuente[25] aged AP/HTPB based CSP (86% solid loading) samples at 65 °C for 128 days. Ageing was monitored through glass transition temperature and its range (onset & end of the peak) using DSC. Both the parameters showed a continuous increase with ageing time. They also found a good correlation between the glass transition temperature range and Young's modulus obtained from samples aged under the same condition. However, Cerri et al.'s[26] DSC study of AP/Al/HTPB based CSPs showed an insignificant change in glass transition temperature with ageing. DSC thermograms indicate changes in the glass-to-rubber transition temperature associated with the mobility unrestricted segments of the binder system.

de la Fuente and Rodrıguez[24] isothermally aged propellant samples at 40, 60 and 80 °C for 5000 h and monitored the changes in dynamic mechanical properties: storage modulus and damping efficiency. They observed different ageing rates for samples obtained from inner and outer layers of the propellant block. Storage modulus data indicated different ageing rates for temperature below and above 60 °C. However, damping efficiency showed linear variation over the entire temperature range.

Cerri et al.[27] observed the effect of accelerated ageing (isothermal, at 60–90 °C, up to 300 days) on two different AP/Al/HTPB based CSPs using DMA in torsion mode. Loss factor curves for both the types had two peaks. The first peak appearing at lower temperature correlated with the peak of DSC thermogram. The second peak was related to the glass-to-rubber transition at higher temperature and was influenced by mobility restricted segments of the binder system, presence of fillers and their interaction with the binder. This analysis suggested that the increase in the chain scission and the cross-linking of binder chains were the two competing processes responsible for the ageing.

4.2.2. Hygro-chemical ageing

The diffusion/absorption of ambient moisture or water may severely affect the mechanical properties of the composite solid propellant and the adhesion properties at the propellant-liner interface. During the mixing process, AP is most susceptible to moisture contamination since it is a hygroscopic inorganic salt which is soluble in water. Moreover, finer (tens of micron order) AP particles are used to obtain higher burn rate. Therefore, moisture contamination is minimized by drying AP in bulk before the mixing process. Ineffective drying may lead to agglomeration (increase in mean particle diameter) during mixing and burn rate degradation. Further, longer drying period are practiced when ammonium oxalate (hygroscopic) is added to AP for reducing the burn rate of the propellant.[93] McDonald et al.[35] studied the moisture effect on the burn rate and surface morphology (using optical microscopy and SEM) of aluminized CSP using finer AP particle. Propellant samples were initially aged at 70 °C for 10 days and at different levels of humidity before the above examination. They suggested that the decrease in the burn rate were due to increase in mean diameter of AP particle size and the corresponding decrease in the effective surface area of the particle.

During the curing process, the absorbed moisture reacts with the curing agent which leads to incomplete curing and subsequently the propellant does not achieve the required tensile strength after the cure.[94] In a typical storage condition, the trapped moisture/water vapor concentration at the core of the grain would be equivalent to ≈15% relative humidity, however, the storage ambient would be at ≈30% relative humidity at 24 °C.[95] During the storage period, the diffused moisture/water vapor reacts with the polymer and the existing cross-links are broken (hydrolysis), resulting in the change in mass molecular distribution and decrease of strength and stiffness of the propellant. The two possible sites for hydrolysis are the double bond of HTPB polymer backbone and the ionic bond at binder/filler interface. Iqbal and Liang[93] have suggested that double bond of HTPB polymer backbone is least affected by hydrolysis. Nevertheless, double bonds of HTPB become susceptible to hydrolysis post oxygen attack. Further, hydrolysis would also lead to chain splitting in the presence of moderate to high humidity. Chang et al.[95] developed 2D numerical model (finite volume) to study the diffusion of moisture over long time period (up to 10 years) in Nike-Hercules rocket motor and subsequent chemical reaction. They observed significant moisture penetration from outer surface to the core within 1 year.

4.3. Ageing studies on binder systems

Many researchers studied ageing behavior of the binder system alone since the CSP ageing was dominated by the degradation of binder which is susceptible to oxidation due to unsaturation in the polymer structure. These studies were also useful in understanding the ageing in insulator, present at the interface between CSP grain and rocket case. Deuri and Bhowmick[96] studied HTPB based binder systems with different levels of initial cross-link density, obtained by varying the amount of curing agent. Samples were aged at 100, 125 and 150 °C up to six days and changes in hardness, elongation, tensile strength and tear strength were observed. No specific trends were found for hardness and elongation, but strength increased with ageing time & temperature. The activation energy of the degradation process was estimated as 50–65 $kJ\cdot mol^{-1}$.

Akbaş et al.[97] studied the thermal ageing of HTPB binders between 50 and 100 °C for 240 days. They monitored the changes in viscosity, functional end-groups, molecular weight, elastic modulus & elongation due to the ageing. They reported increase in viscosity, molecular weight, elastic modulus and decrease in elongation indicating embrittlement. They also indicated oxidative degradation of HTPB in which the rate of cross-link formation was higher than the rate of chain scission reaction.

Celina et al.[82,98] conducted isothermal ageing of cured HTPB at different temperatures between 25 and 125 °C. Changes in various parameters including modulus, elongation, density and oxygen consumption & permeation were monitored. Oxidation was inferred as the degradation mechanism. In thicker samples, it was restricted by diffusion of oxygen which led to heterogeneous ageing: different degree of deterioration from exterior points to interior points in the same sample. Using chemi-luminescence, Sinturel and Billingham[99] also confirmed heterogeneous diffusion limited oxidative (DLO) degradation in HTPB. Arrhenius plot obtained from the above degradation monitoring parameters showed curvature, indicating different activation energies (70 & 120 $kJ\cdot mol^{-1}l$) for lower and higher temperature ranges.

5. Monitoring of age in solid propellant rocket motors

In the previous sections, different types of ageing in composite solid propellant rocket motors, its sources and mechanisms have been reviewed. It has been explained how the ageing causes significant deterioration in the propellant and propellant-liner interface. Moreover, the deterioration limits the service-life of the rocket motor and needs to be quantified for ensuring the intended operation of the system. In literature, the changes in physical, mechanical and ballistic properties of the propellant have been used as passive means to monitor the ageing. Samples are drawn from the stored propellant/grain periodically and the above properties are measured and compared against the unaged propellant properties. However, the above method of periodic testing is effective for monitoring physical and chemical ageing. Sub-scale system level testing, analysis and active health monitoring are required to capture the cumulative damage effects and the deterioration of interfaces in the stored rocket.

5.1. Effect of ageing on the physical properties

Hardness measurement is used as a standard quality check for stored propellant grains. The propellant becomes harder with thermo-chemical ageing and softens due to hygro-thermal ageing.[88,100,101] Low temperature storage makes propellant harder, nevertheless, the effects of physical ageing on the propellant hardness needs to be explored. Further, stress cycling effects on the propellant hardness requires detailed study. Rao et al.[102] have developed an in-situ technique, based on flat punch indentation, to correlate/evaluate the mechanical properties (modulus, strength and percentage elongation) of the stored grain. Optical microscopy and scanning electron microscopy have been used for qualitative investigation of the surface morphology of ageing propellants. However, these studies are inconclusive and it requires a newer approach. In the following sections, the ageing effects on the mechanical and ballistic properties of the propellant have been discussed along with the health monitoring method for the stored grains.

5.2. Effect of ageing on the mechanical properties

Various tensile and viscoelastic properties are measured and used while designing the propellant grain and performing the stress/strain analysis of the grain with the case, liner and insulator. Thermo-chemical ageing leads to embrittlement of the propellant which involves stiffening (increase in modulus) of the propellant at the cost of reduction in its percentage elongation. This is accompanied by an appreciable increase in the tensile strength and decay in dilatation properties of the propellant.[34,70,88,103] Stress cycling effects on the tensile properties of an ageing propellant needs to be explored. Ageing effects on the viscoelastic properties are quantified through sinusoidal strain or stress application (dynamic mechanical analysis), creep and relaxation testing of unaged and aged samples. Loss factor curve flattens, β transition temperature decreases and storage modulus curve shifts upward (after β transition temperature) with the ageing.[27] Long period creep/relaxation testing of propellant was not reported in the literature primarily due to the difficulty in maintaining low humidity level for the long period. Recently, Naseem[104] has developed the short period creep-recovery testing procedure for composite solid propellant and studied the ageing effects on various creep properties at three stress levels. Higher rate of deterioration in all the creep properties were observed in the initial phases of ageing due to the availability of higher concentration of reactants. Creep coefficient, maximum creep strain and recovery coefficient have more than 50% decay at the end of 5 years of equivalent natural age for the three stress levels. Hygro-chemical ageing effects on the tensile and viscoelastic properties requires attention of the researchers as they are not well-studied.

5.3. *Health monitoring of ageing motor*

The propellant-liner-insulation interfaces have some features of adhesively bonded interfaces. Double cantilever sandwich tests, tensile bond strength tests and peel tests are used to measure the interface bond strength. Accelerated ageing studies on the interfaces using wheel-peel test and tensile bond strength tests have shown cohesive failure in the propellant.[73] Peel test of a propellant-liner interface by Toulemonde et al.[105] also indicated cohesive fracture in propellant. Zhou et al.[72,106] simulated the debonding at the interface using cohesive zone model and investigated the same using experiments. Their results demonstrated that cohesive zone models can simulate the initiation and propagation of interface cracks in mode I. This is applicable for any pre-existing cracks at the interface and their propagation over a period of time. The extensive review by Zhou et al.[72] on the adhesively bonded interface in a solid rocket motor details the various complex phenomena involved in degradation of the propellant-liner interfaces. Residual thermal stresses accumulated during the cool down process in the rocket motor are one of the prime factors in determining the useful life of a rocket motor.

Sub-scale motors were used to measure the actual strains and stresses in the full-scale motor, using strain gauges, photoelasticity, X-ray testing, ultrasonic testing and destructive tests and firing tests. It was observed that high stresses and strains (caused by large temperature fluctuations) contribute to large amount of cumulative damage. In case bonded propellant grain, these stresses were proportional to the difference between the thermal expansion co-efficient of propellant and case. Tussiwand et al.[107] considered non-destructive and built in methods for ageing state determination of solid rocket motors. Dual bond stress and temperature (DBST) sensors were embedded onto the inner side of the rocket motor case. The motor case is insulated and the response of DBST sensors in the insulated case was measured by applying known temperature history and the values were recorded. After propellant casting, the temperature cycle was repeated and stresses were recorded. Stress data obtained after storing the motors at different temperatures and durations indicated good correlation with the Arrhenius equation.

6. Conclusions and suggestions

A comprehensive review on the ageing of AP/HTPB based composite solid propellants have been presented, along with the evolution of this propellant. Physical ageing is a concern for low temperature storage conditions and should be studied to account for its effects on the propellant properties. Researchers have shown that the migration of plasticizer can be minimized and have small impact on the shelf-life of the grain. However, it could adversely affect the adhesion properties of the propellant liner interface. Further, the diffusion of humidity in propellant grain and the associated hygro-chemical ageing need to be explored in detail.

Substantial amount of research have been conducted on thermo-chemical ageing of different types of composite solid propellants and efforts were made to understand the respective degradation mechanisms. Results showed that the thermo-chemical ageing makes propellant harder, stiffer and significantly reduces its strain carrying capacity. These deteriorations lead to failure (cracks & debond) of grain during shelf-life and the aged propellants become incapable of resisting high strain rate loading while motor firing.

Cumulative damage in the grain due to various stress fields have been extensively studied and subsequently service-life prediction models were proposed. Effects of thermo-chemical ageing have also been included in these prediction models. However, the deterioration of propellant-liner interface has not been considered which is critical in larger motors. Moreover, the cumulative damage due to vibratory loads has not been adequately addressed in these models due to the nonavailability of propellant mechanical response under forced vibration. Better sensors and techniques are required for the effective health monitoring of the stored motors.

Aforementioned review presents a comprehensive outline of many advancements which have been made in understanding the ageing in AP/HTPB (both non-aluminized and aluminized) based composite solid propellants. However, there are still following problems and should be addressed in the future.

- Physical ageing in composite solid propellants at low temperature storage condition and its influence on mechanical and ballistic properties
- Modeling of humidity diffusion in the propellant grain, its impact on AP particles and subsequent effects on the propellant properties
- Propellant mechanical characterization under dynamic loading and development of the respective constitutive material models
- Study of slump due to small acceleration loads during transportation and high acceleration loads during flight
- Improved sub-system level modeling & testing for propellant-liner interface to achieve better correlation with full scale motor
- Detailed study of hygro-chemical ageing of the propellant and its interaction with other chemical ageing modes
- Effects of chemical ageing on the ballistic properties of the propellant
- Development of a comprehensive laboratory ageing methodology and safe-life prediction model which effectively captures actual grain service condition, consists of different storage locations for different time periods and intermittent transportation/handling
- Development of sensors and techniques for active health monitoring of stored grains

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

1. Benson T. Brief history of rockets. http://www.grc.nasa.gov/www/k-12/TRC/Rockets/history_of_rockets.html; 2010.
2. Jain SR. Solid propellant binders. *J Sci Ind Res.* 2002;61:899–911.
3. Nagappa R. *Evolution of Solid Propellant Rockets in India.* New Delhi: DRDO Monographs/Special Publications Series; 2014.
4. Davenas A. *Solid Rocket Propulsion Technology.* Oxford: Pergamon Press Ltd.; 1993.
5. Mukunda HS. *Understanding Aerospace Chemical Propulsion.* Bangalore: Interline Publishing; 2004.
6. Bunyan P, Cunliffe AV, Davis A, Kirby FA. The degradation and stabilisation of solid rocket propellants. *Polym Degrad Stabil.* 1993;40(2):239–250.
7. Davenas A. Development of modern solid propellants. *J Propul Power.* 2003;19(6): 1108–1128.
8. Ang HG, Pisharath S. *Energetic Polymers: Binders and Plasticizers for Enhancing Performance.* Weinheim: John Wiley & Sons; 2012.

9. Trache D, Klapotke TM, Maiz L, Abd-Elghany M, DeLuca LT. Recent advances in new oxidizers for solid rocket propulsion. *Green Chem*. 2017;19(20):4711–4736.
10. Oommen C, Jain S. Ammonium nitrate: a promising rocket propellant oxidizer. *J Hazard Mater*. 1999;67(3):253–281.
11. Jos J, Mathew S. Ammonium nitrate as an eco–friendly oxidizer for composite solid propellants: promises and challenges. *Crit Rev Solid State Mater Sci*. 2017;42(6): 470–498.
12. Dendage PS, Sarwade DB, Asthana SN, Singh H. Hydrazinium nitroformate (HNF) and HNF based propellants: a review. *J Energetic Mater*. 2001;19(1):41–78.
13. Kumar P. An overview on properties, thermal decomposition, and combustion behavior of ADN and ADN based solid propellants. *Def Technol*. 2018;14(6): 661–673.
14. Boyd AB, Burkes WM, Medford JE. Grain design and development problems for very large rocket motors. In: Summerfield M, ed. *Solid Propellant Rocket Research*. vol. 1. AIAA; 1960:3–31.
15. van Breugel K. Urgency and challenges of ageing in science and engineering. In: van Breugel K, Koleva D, Beek T, eds. *The Ageing of Materials and Structures*. Springer International Publishing; 2018:3–13.
16. Gates T. The physical and chemical ageing of polymeric composites. In: Martin R, ed. *Ageing of Composites*. CRC Press; 2008:3–33.
17. Kelley FN. In: Boyars C, Klager K, eds. *Solid Propellant Mechanical Properties Testing, Failure Criteria, and Aging*. American Chemical Society Publications; 1969:188–243.
18. Kishore K, Sridhara K. *Solid Propellant Chemistry*. New Delhi: DRDO Monographs/ Special Publications Series; 1999.
19. Probster M, Schmucker RH. Ballistic anomalies in solid rocket motors due to migration effects. *Acta Astronaut*. 1986;13(10):599–605.
20. Tormey JF, Britton SC. Effect of cyclic loading on solid propellant grain structures. *AIAA J*. 1963;1(8):1763–1770.
21. Whitehouse A. *Structural Assessment of Solid Propellant Grains*. 1997. AGARD-AR-350.
22. Struik LCE. *Physical Aging in Amorphous Polymers and Other Materials*. Amsterdam: Elsevier Scientific Press; 1978.
23. Siegmann A, Cohen D, Narkis M. Polyurethane elastomers containing polybutadiene and aliphatic diols: structure-property relationships. *Polym Eng Sci*. 1987;27(15):1187–1194.
24. de la Fuente JL, Rodríguez O. Dynamic mechanical study on the thermal aging of a hydroxyl-terminated polybutadiene-based energetic composite. *J Appl Polym Sci*. 2003;87(14):2397–2405.
25. de la Fuente JL. An analysis of the thermal aging behaviour in high-performance energetic composites through the glass transition temperature. *Polym Degrad Stabil*. 2009;94(4):664–669.
26. Cerri S, Bohn MA, Menke K, Galfetti L. Ageing behaviour of HTPB based rocket propellant formulations. *Cent Eur J Energ Mat*. 2009;6(2):149–165.
27. Cerri S, Bohn MA, Menke K, Galfetti L. Aging of HTPB/Al/AP rocket propellant formulations investigated by DMA measurements. *Propellants, Explos Pyrotech*. 2013;38(2):190–198.
28. Bihari BK, Wani VS, Rao NPN, Singh PP, Bhattacharya B. Determination of activation energy of relaxation events in composite solid propellants by dynamic mechanical analysis. *Def Sci J*. 2014;64(2):173–178.
29. Nguyen TQ. In: Meyer T, Keurentjes J, eds. *Polymer Degradation and Stabilization*. John Wiley & Sons, Ltd; 2008:757–831.
30. Dee L, Emmanuel L, Fiske M, Ninomiya L. *Solid Propellant Ingredient Migration Studies*. 1982. AFRPL-TR-82-030.
31. Venkatesan D, Srinivasan M, Reddy KA, Pendse VV. The migration of plasticizer in solid propellant grains. *Polym Int*. 1993;32(4):395–399.
32. Gottlieb L, Bar S. Migration of plasticizer between bonded propellant interfaces. *Propellants, Explos Pyrotech*. 2003;28(1):12–17.
33. Libardi J, Ravagnani SP, Morais AMF, Ca R. Study of plasticizer diffusion in a solid rocket motors bondline. *J Aero Technol Manag*. 2009;1(2):223–229.
34. Judge MD. An investigation of composite propellant accelerated ageing mechanisms and kinetics. *Propellants, Explos Pyrotech*. 2003;28(3):114–119.
35. McDonald BA, Rice JR, Kirkham MW. Humidity induced burning rate degradation of an iron oxide catalyzed ammonium perchlorate/HTPB composite propellant. *Combust Flame*. 2014;161(1):363–369.
36. Gligorijevic N, Rodic V, Jeremic R, Zivkovic S, Subotic S. Structural analysis procedure for a case bonded solid rocket propellant grain. *Sci Technol Rev*. 2011; 61(1):1–9.
37. Sutton GP, Biblarz O. *Rocket Propulsion Elements*. New Jersey: John Wiley & Sons, Inc.; 2017.
38. Bills Jr K, Svob G, Planck R, Eriksson T. A cumulative-damage concept for propellant-liner bonds in solid rocket motors. *J Spacecraft Rockets*. 1966;3(3): 408–412.
39. Kunz R. Continuum damage mechanics modeling of solid propellant. In: *44th AIAA/ ASME/SAE/ASEE Jt. Propuls. Conf. Exhib.*. 2008. AIAA 2008-4973.
40. Fitzgerald JE, Hufferd WL. Handbook for the Engineering Structural Analysis of Solid Propellants. In: . CPIA Publication No. 214; 1971. AD0887478.
41. Noel JS. *Solid Propellant Grain Structural Integrity Analysis*. 1973. NASA-SP-8073.
42. Adel WM, Guo-zhu L. Study of cooldown thermal loading effect on the bore deformation of viscoelastic solid propellant grain. In: *53rd AIAA/SAE/ASEE Jt. Propuls. Conf.*. 2017. AIAA 2017-4692.
43. Williams ML, Blatz PJ, Schapery RA. *Fundamental Studies Relating to Systems Analysis of Solid Propellants*. Guggenheim Aeronautical Laboratory, California Institute of Technology; 1961.
44. Durelli A, Parks V. Photoelasticity methods to determine stresses in propellant-grain models. *Exp Mech*. 1965;5(2):33–45.
45. Sampson RC, Campbell DM. Contributions of photoelasticity to evaluation of solid propellant motor integrity. *J Spacecraft Rockets*. 1966;3(4):477–483.
46. Knauss WG. Displacements in an axially accelerated solid propellant rocket grain. In: *20th Meeting Bulletin, JANAFAN Panel on Physical Properties of Solid Propellants*. vol. 1. Solid Propellant Information Agency, Johns Hopkins University; 1961: 175–186.
47. Lianis G. Stresses and strains in solid propellants during storage. *ARS J*. 1962;32(5): 688–692.
48. Herrmann LR, Tamekuni M. Horizontal slump of solid propellant motors. *AIAA J*. 1965;3(4):696–700.
49. Renganathan K, Rao B, Jana M. Slump estimation of cylindrical segment grains of a typical rocket motor under vertical storage condition. *Trends Appl Res*. 2006;1(1): 97–104.
50. Nawaz Q, Nizam F. Viscoelastic response of HTPB based solid fuel to horizontal and vertical storage slumping conditions and it's affect on service life. In: *Key Engineering Materials*. vol. 510. Switzerland: Trans Tech Publication; 2012:22–31.
51. Deng B, Tang G, Shen Z. Structural analysis of solid rocket motor grain with aging and damage effects. *J Spacecraft Rockets*. 2015;52(2):331–339.
52. Ostrem FE. *Transportation and Handling Loads*. 1971. NASA-SP-8077.
53. Wang Z, Qiang H, Wang G, Huang Q. Tensile mechanical properties and constitutive model for HTPB propellant at low temperature and high strain rate. *J Appl Polym Sci*. 2015;132(24).
54. Yılmaz O, Kuran B, Ozgen GO. Reliability assessment of solid-propellant rocket motors under storage and transportation loads. *J Spacecraft Rockets*. 2017;54(6): 1356–1366.
55. Heller RA, Kamat MP, Singh MP. Probability of solid-propellant motor failure due to environmental temperatures. *J Spacecraft Rockets*. 1979;16(3):140–146.
56. Geckler RD. Thermal stresses in solid propellant grains. *J Jet Propuls*. 1956;26(2): 93–97.
57. Mahmoudi H, Atefi G. Analytical solution for thermal stresses in a hollow cylinder under periodic thermal loading. *Proc Inst Mech Eng C J Mech Eng Sci*. 2012;226(7): 1705–1724.
58. Zwick S. Thermal stresses in an infinite, hollow case-bonded cylinder. *J Jet Propuls*. 1957;27(8):872–876.
59. Zak AR. Structural analysis of realistic solid propellant materials. *J Spacecraft Rockets*. 1968;5(3):270–275.
60. Tunc B, Ozupek S, Podnos E, Arkun U. Thermal cyclic stress analysis of a solid rocket motor. *J Spacecraft Rockets*. 2019;56(1):179–189.
61. Thangjitham S, Heller RA. Stress response of rocket motors to environmental thermal loads. *J Spacecraft Rockets*. 1986;23(5):519–526.
62. Heller RA, Singh MP. Thermal storage life of solid-propellant motors. *J Spacecraft Rockets*. 1983;20(2):144–149.
63. Gligorijevic N, Zivkovic S, Subotic S, Rodic V, Gligorijevic I. Effect of cumulative damage on rocket motor service life. *J Energetic Mater*. 2015;33(4):229–259.
64. Gligorijevic N, Rodic V, Pavkovic B, Bogdanov J, Zivkovic S, Bajic Z. Effect of cyclic loads on structural damage of rocket propellant grain. *Sci Technol Rev*. 2019;69(2): 8–16.
65. Zibdeh HS, Heller RA. Rocket motor service life calculations based on the first-passage method. *J Spacecraft Rockets*. 1989;26(4):279–284.
66. Janajreh I, Heller RA, Thangjitham S. Safety index approach to predicting the storage life of rocket motors. *J Spacecraft Rockets*. 1994;31(6):1072–1078.
67. Margetson J, Wong FC. *Service Life Prediction of Solid Rocket Propellant Motors Stored in a Random Thermal Environment*. 1997. AGARD-CP-586.
68. Ozupek Ş. Computational procedure for the life assessment of solid rocket motors. *J Spacecraft Rockets*. 2010;47(4):639–648.
69. Yıldırım H, Ozüpek Ş. Structural assessment of a solid propellant rocket motor: effects of aging and damage. *Aero Sci Technol*. 2011;15(8):635–641.
70. Layton LH. *Chemical Structural Aging Studies on an HTPB Propellant*. 1975. AFRPLTR-75-13.
71. Rodic V. Case bonded system for composite solid propellants. *Sci Technol Rev*. 2007; 57(3-4):77–82.
72. Zhou QC, Xu JS, Chen X, Zhou CS. Review of the adhesively bonded interface in a solid rocket motor. *J Adhes*. 2016;92(5):402–428.
73. Kakade SD, Navale SB, Narshiman VL. Studies on interface properties of propellant liner for case-bonded composite propellants. *J Energetic Mater*. 2003;21(2):73–85.
74. Larson EL. *A Review of the Minuteman Propulsion Surveillance Program for Assessing Rocket Motor Service Life*. 1965:AD467048.
75. Lund E. Minuteman long range service life analysis overview. In: *12th Propuls. Conf.*. 1976:716.
76. Liu EK, McCamey RK. Lessons learned in service life prediction. In: Mallinson L, ed. *Ageing Studies and Lifetime Extension of Materials*. Springer; 2001:529–536.
77. Shekhar H. Prediction and comparison of shelf life of solid rocket propellants using Arrhenius and Berthelot equations. *Propellants, Explos Pyrotech*. 2011;36(4): 356–359.
78. Laidler KJ. The development of the Arrhenius equation. *J Chem Educ*. 1984;61(6): 494–498.
79. Kishore K, Verneker VRP, Prasad G. Mechanism of aging of composite solid propellants. *Combust Flame*. 1979;36:79–85.
80. Celina M, Gillen KT, Assink RA. Accelerated aging and lifetime prediction: review of non-Arrhenius behaviour due to two competing processes. *Polym Degrad Stabil*. 2005;90(3):395–404.
81. Kaushal K, Verneker VRP, Prasad G. Storage stability of solid rocket fuel. 1. Effect of temperature. *Fuel*. 1977;56(3):292–294.
82. Celina M, Minier L, Assink RA. Development and application of tools to characterize the oxidative degradation of AP/HTPB/Al propellants in a propellant reliability study. *Thermochim Acta*. 2002;384(1-2):343–349.

83. Flynn JH. Thermal analysis kinetics-problems, pitfalls and how to deal with them. *J Therm Anal*. 1988;34(1):367–381.
84. Flynn JH. Lifetime prediction for polymers from thermal analytical experiments problems and how to deal with some of them. *Thermochim Acta*. 1988;134: 115–120.
85. Flynn JH. A critique of lifetime prediction of polymers by thermal analysis. *J Therm Anal*. 1995;44(2):499–512.
86. Husband DM. Use of dynamic mechanical measurements to determine the aging behavior of solid propellant. *Propellants, Explos Pyrotech*. 1992;17(4):196–201.
87. Budrugeac P, Segal E. Thermal analysis in the evaluation of the thermal lifetime of solid polymeric materials. *Thermochim Acta*. 1992;211:131–136.
88. Naseem H, Murthy H, Ramakrishna PA. Accelerated ageing of composite solid propellants under cyclic temperature variations. *J Energetic Mater*. 2020:1–27. https://doi.org/10.1080/07370652.2020.1815899.
89. Christiansen AG, Layton LH, Carpenter RL. HTPB propellant aging. *J Spacecraft Rockets*. 1981;18(3):211–215.
90. Olson DB, Gill RJ. *Propellant Aging Research*. 1987. AFRPL-TR-86-096.
91. Kishore K, Verneker VRP, Prasad G. Mechanism of the oxidative degradation of binder during the aging of composite solid propellant. *J Appl Polym Sci*. 1979;24: 589–593.
92. Hocaoğlu O, Özbelge T, Pekel F, Özkar S. Aging of HTPB/AP-based composite solid propellants, depending on the NCO/OH and triol/diol ratios. *J Appl Polym Sci*. 2001;79(6):959–964.
93. Iqbal MM, Liang W. Modeling the moisture effects of solid ingredients on composite propellant properties. *Aero Sci Technol*. 2006;10(8):695–699.
94. Gustavson C, Greenlee TW, Ackley AW. Bonding of composite propellant in cast-in-case rocket motors. *J Spacecraft Rockets*. 1966;3(3):413–418.
95. Chang S, Han S, Malone B. Numerical analysis of moisture propagation and chemical reaction in a solid propellant. In: *36th AIAA/ASME/SAE/ASEE Jt. Propuls. Conf. Exhib.*. 2000. AIAA 2000-3180.
96. Deuri AS, Bhowmick AK. Influence of ageing on strength properties and morphology of fracture surface of hydroxy terminated polybutadiene rubber. *Mater Chem Phys*. 1987;18(1-2):35–48.
97. Akbaş A, Aksoy S, Hasırcı N. Effects of thermal ageing on the properties and lifetime prediction of hydroxyl-terminated polybutadiene. *Polymer*. 1994;35(12): 2568–2572.
98. Celina M, Graham A, Gillen K, Assink R, Minier L. Thermal degradation studies of a polyurethane propellant binder. *Rubber Chem Technol*. 2000;73(4):678–693.
99. Sinturel C, Billingham NC. A theoretical model for diffusion-limited oxidation applied to oxidation profiles monitored by chemiluminescence in hydroxy-terminated polybutadiene. *Polym Int*. 2000;49(9):937–942.
100. Davis D. Use of dilatation in understanding composite propellant aging. In: *37th AIAA/ASME/SAE/ASEE Jt. Propuls. Conf. Exhib.*. 2001. AIAA 2001-6040.
101. Adel WM, Liang G. Service life prediction of AP/Al/HTPB solid rocket propellant with consideration of softening aging behavior. *Chin J Aeronaut*. 2019;32(2): 361–368.
102. Rao NP, Solanke C, Bihari BK, Singh PP, Bhattacharya B. Evaluation of mechanical properties of solid propellants in rocket motors by indentation technique. *Propellants, Explos Pyrotech*. 2016;41(2):281–285.
103. Kadiresh PN, Sridhar BTN. Experimental evaluation and simulation on aging characteristics of aluminised AP-HTPB composite solid propellant. *Mater Sci Technol*. 2008;24(4):406–412.
104. Naseem H. *Accelerated Thermo-Chemical Ageing Studies on Composite Solid Propellants*. India: IIT Madras; 2020.
105. Toulemonde PA, Diani J, Gilormini P, Desgardin N, Neviere R. Propellant cohesive fracture during the peel test of a propellant/liner structure. *J Adhes*. 2018;94(8): 657–666.
106. Zhou QC, Ju YT, Wei Z, Han B, Zhou CS. Cohesive zone modeling of propellant and insulation interface debonding. *J Adhes*. 2014;90(3):230–251.
107. Tussiwand G, Eineder L, Mussbach G, Bohn MA. Non-destructive ageing state determination of solid rocket motors charge. In: *8th Eur. Workshop Struct. Health Monitoring*. EWSHM 2016); 2016:5–8.

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